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Development of a Strategy for Sampling Tree Rings

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Development of a Strategy for Sampling Tree Rings

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March 1979

DEVELOPMENT OF A STRATEGY FOR SAMPLING TREE RINGS

by

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FOREWORD

Protection of the environment requires effective regulatory actions which are based on sound technical and scientific information. This information must include the quantitative description and linking of pollutant sources, transport mechanisms, interactions, and resulting effects on man and his environment. Because of the complexities involved, assessment of specific pollutants in the environment requires a total systems approach which transcends the media of air, water, and land. The Environmental Monitoring and Support Laboratory-Las Vegas contributes to the formation and enhancement of a sound monitoring data base for exposure assessment through programs designed to:

- develop and optimize systems and strategies for monitoring pollutants and their impact on the environment

- demonstrate new monitoring systems and technologies by applying them to fulfill special monitoring needs of the Agency's operating programs

This report documents the development of a strategy to retrospectively monitor pollutant levels in air by measuring arsenic concentrations in samples of wood obtained from annual growth rings of trees in the vicinity of a smelter. Such information can provide a basis to assess the relative risks to the health and well-being of a local population exposed to environmental hazards and to aid in the improvement of our environmental quality. The advantage of such a program will permit us to assess the effectiveness of past environmental control technologies with those of the future and establish an environmental baseline with which to compare future control technologies.

Federal and local agencies interested in assessing past exposures of local populations to hazardous or carcinogenic materials released to the environment will find this study useful. In addition, the information it provides may be used to determine the effectiveness of newer control methodologies. Additional information about the study may be obtained by contacting the Monitoring Systems Research and Development Division, Environmental Monitoring and Support Laboratory, Las Vegas, Nevada.

George B. Morgan
Director
Environmental Monitoring and Support Laboratory
Las Vegas

ABSTRACT

A method for determining retrospective pollution levels has been investigated. This method relates arsenic concentration in tree rings to arsenic-in-air concentrations based qualitatively on arsenic emissions from a nearby smelter, corrected for climatological and meteorological effects. To evaluate the validity of the method, a unique pollution study area was identified and characterized in detail. Several select trees were sampled and the arsenic concentration determined by neutron activation analysis. These concentrations were compared to certain known phases in the production history of the smelter, coupled with the expected climatology and meteorology of the area. Positive correlations were found thus satisfying the goals of the preliminary project. Major problems encountered were low arsenic concentrations and an inadequate number of samples. Recommendations for future studies are given.

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I am also greatly indebted to many staff members of the Puget Sound Air Pollution Control Agency for their valuable input, especially in historical documentation.

For allowing me to freely choose trees for sampling on their property, I am equally indebted to Mr. and Mrs. Alan Houston and Mr. Lewis Duncan. Their interest in this project and enthusiasm to cooperate were heart-warming.

Finally, I wish to acknowledge the input of Dr. William Kreiss, a meteorologist with Physical Dynamics, Inc., of Seattle. His general guidance and encouragement were appreciated and his meteorological expertise made Section 9 possible.

SECTION 1

INTRODUCTION

The primary difficulty in relating the incidence and causation of human disease to environmental factors in epidemiological studies results from the lack of good retrospective data. Because many diseases develop over a period of years, it is of major importance to determine an accurate chronology of those items that lead directly to the initiation of the disease. Few accurate methods exist, especially in the area of pollution-caused diseases. This project is a first step in the development of such a method.

The technique of dendrochronology is most often used to estimate the age of a tree. By carefully evaluating the successive layers of xylem growth, or "tree rings" as they are commonly called, from the pith to the cambium, the age of a tree can be accurately determined. This technique is widely known and used. Also, local climatic history can be reconstructed from a detailed analysis of tree rings. In general, the width of the ring is related to the precipitation and temperature exposure. In addition, patterns of varying ring widths are established over a period of years due to exposure to various weather conditions, and these can be traced from tree to tree in a given climatic area. These patterns have been used to date items ranging from the age of windfalls to the age of objects constructed from wood.

Directly related to this, but even less well known, is the fact that other information is also stored in the rings of xylem growth. As will be discussed in this report, some trace chemical elements known to be nonessential for tree growth are found in the xylem. Furthermore, the concentration of these nonessential elements in tree rings can vary from year to year, and it has been demonstrated that they can be related to a pollution source many kilometers away. Such elements possibly enter the tree via the soil by rainout or fallout.

The development of this method for retrospective determination of pollutant levels is based on the above facts. The subject of this study is the demonstration that the concentration of some pollutants in the rings is proportional to the pollution to which the trees are exposed.

SECTION 2

SUMMARY

The concentration of arsenic in tree rings was found to be proportional to the annual emission of arsenic from a copper smelter 8 kilometers away from the trees. The study site is on an island, and so transport from the stack by air has been validated. Although positive correlations were made, several anomalies exist that need to be answered. An apparent lag of one to two growing seasons in the uptake of arsenic from the soil was identified in tree rings taken from lower portions of the tree. On the other hand, no lag was noted between production output from the smelter and tree rings taken from higher elevations in the tree, suggesting a direct uptake from the air through the needles. Although the evidence is not conclusive, some species of trees appear to behave differently from others, but all species evaluated showed the lag effect in samples collected nearest the root system.

SECTION 3

RECOMMENDATIONS

The data contained in this report suggest that tree ring analyses are valid indicators of past pollution levels. This presents the possibility of retrospective evaluation of pollution. Several important steps must be taken, however, before the method can be demonstrated to be quantitative.

First, pollutants other than arsenic need to be evaluated for this study area. Second, a larger number of sample trees needs to be evaluated. Third, other species of trees need to be evaluated in greater detail than was possible in this study. Fourth, duplicate increment samples should be taken during the sampling stage, and one of these should be mounted, polished and varnished in order to eliminate or at least minimize ring-counting errors. Fifth, definite climatological-growth relationships need to be developed, a major factor in this type of study. Finally, higher neutron flux should be used for the analysis to maximize the pollutant activity in the rings.

Whereas this study was conducted in a short time and on a limited budget, future studies should be extended in time and budget in order to accurately assess all of the possible variables and draw conclusive results.

SECTION 4

BACKGROUND INFORMATION

TREE RING ANALYSIS

The trace element concentrations in the xylem ring of trees are known to be proportional to the elemental concentration in the soil (Lepp, 1975). Early studies (Sheppard and Funk, 1975) have shown that the rings of trees whose roots were exposed to contaminated water in an Idaho river downstream from a mine contained trace-metal concentrations that were directly proportional to the yearly pollution levels of the river and the yearly output of the mine. Tree rings examined in certain Pennsylvania trees (Pillay, 1975) contained concentrations of trace metals known to be present in the local atmosphere, and the observed variations in the rings suggested a relationship proportional to the pollution in the environment. Heavy metal studies by Ault et al. (1970) and Ward et al. (1973) have shown that lead levels in tree rings could be correlated with local traffic density. On the other hand, a detailed study by Szopa et al. (1973) showed that lead levels in oak trees near an abandoned highway continued to register high lead levels after the abandonment, suggesting that direct yearly correlations may be in error. (This study, however, did not consider the possibility of root uptake of lead from the soil.) Finally, unpublished tree-ring data taken by the author on trees located in polluted and unpolluted environments have clearly indicated that certain environmental contaminants present in air pollution are concentrated in tree rings, that the concentrations of these elements appear to be a function of the type of soil in which the tree is located, and that the concentration varies annually.

While all of these results indicate that a relationship may exist between the concentration in the rings and the local environment, a detailed analysis of all relevant variables was needed in order to evaluate the validity of this method as a tool for retrospectively determining pollution levels. This report describes the progress to date concerning the first step in this verification process--a simple demonstration of the correlation between tree-ring concentration and the polluted environment of the tree.

PROBLEM IDENTIFICATION

Several parameters needed to be determined in order to develop this method for use as a technique for retrospective determination of pollution. These included tree-related parameters. Processes related to the uptake, transport, and deposition of trace elements in the tree needed to be understood. Items such as diffusion of trace elements to adjacent rings, the preferential uptake of certain species from the soil, the effects of soil diffusion and leaching, the uptake of the elements directly from the air through broad leaves and needles, all needed to be understood. Equally important were the pollution source-related parameters. An accurate chronology of the source emissions was needed, as well as the various transport processes and mechanisms. In addition, a well-defined meteorological history was mandatory. No one parameter stood out as most important. All were related in one way or another and had a direct effect on the accuracy of the method--hence on the demonstration of the method validity.

A most important first step in the demonstration of the validity of this method was the identification and characterization of an ideal study area. This unique site was found to be located in a second growth area in the Puget Sound of northwestern Washington. The area contained a single major source of pollution, and the only direct means of pollutant transport was by air (Fig. 1). Equally important was the tree-ring concentration/pollution environment correlation mentioned above. This has been verified, at least qualitatively, and the remainder of this report discusses the results.

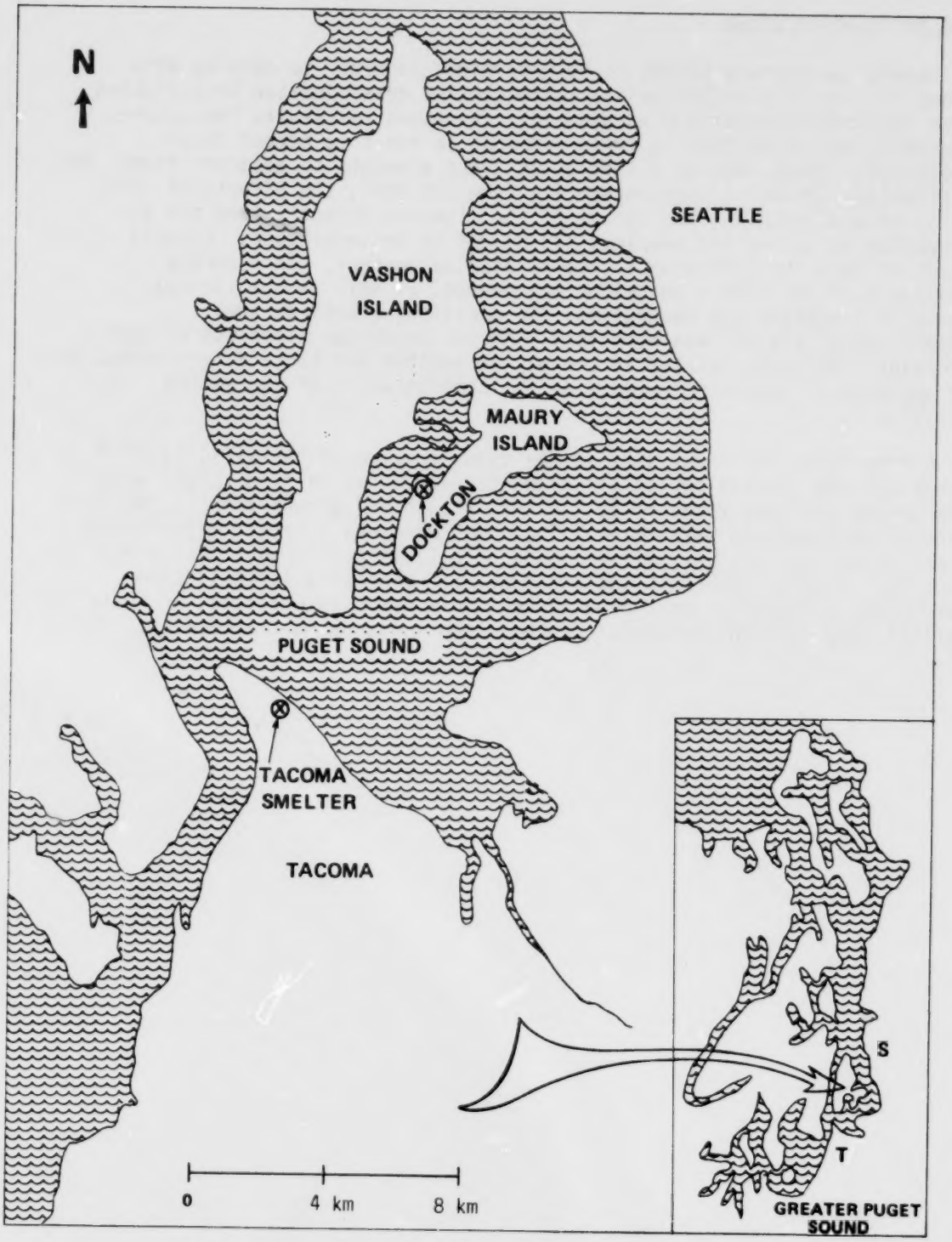

Figure 1. The ASARCO Tacoma smelter study area

SECTION 5

THE ASARCO TACOMA SMELTER STUDY AREA

Several important parameters qualified the selected study area as ideal for this demonstration project. These were related to four distinct factors that substantially reduced the level of error: a well-defined and characterized study system; ideal sampling sites; ideal chemical tracer elements and techniques for the analysis; and an established meteorological history of the area.

UNIQUENESS OF THE STUDY AREA

Much scientific work related to this project, and especially to the overall study area, had been done in the recent past. Tree-ring analyses previously performed by the author had formed the basis for this demonstration project. Detailed studies on the particulate (Nelson and Roberts, 1975) and gaseous (Washington State, 1976) emissions had been conducted; dispersion modeling of the gaseous emission had been accomplished (Cramer et al., 1976); an extensive air pollution monitoring system was in use (Fig. 2); the surrounding water and sediments between the source and the sampling sites on Maury Island (Fig. 2) had been characterized in detail (Crecelius et al., 1975); and many other pollutant-related studies, ranging from arsenic levels in hair and urine (Johnson and Lippman, 1973) to cadmium levels in vegetable gardens (Heilman and Ekuan, 1977), had been conducted. In general, considerable information was available on the selected study area.

UNIQUENESS OF THE SAMPLING SITES

Two distinct sampling sites were identified near the City of Dockton on Maury Island (see Fig. 2). Maury Island and Vashon Island are bridged with a fill area and lie west of Seattle and north of Tacoma, the two major urban areas in Puget Sound. Although close to these cities, they are virtually isolated (ferry connections only). Both islands consist mainly of small farms and second growth timber, have little or no industrial sources, and

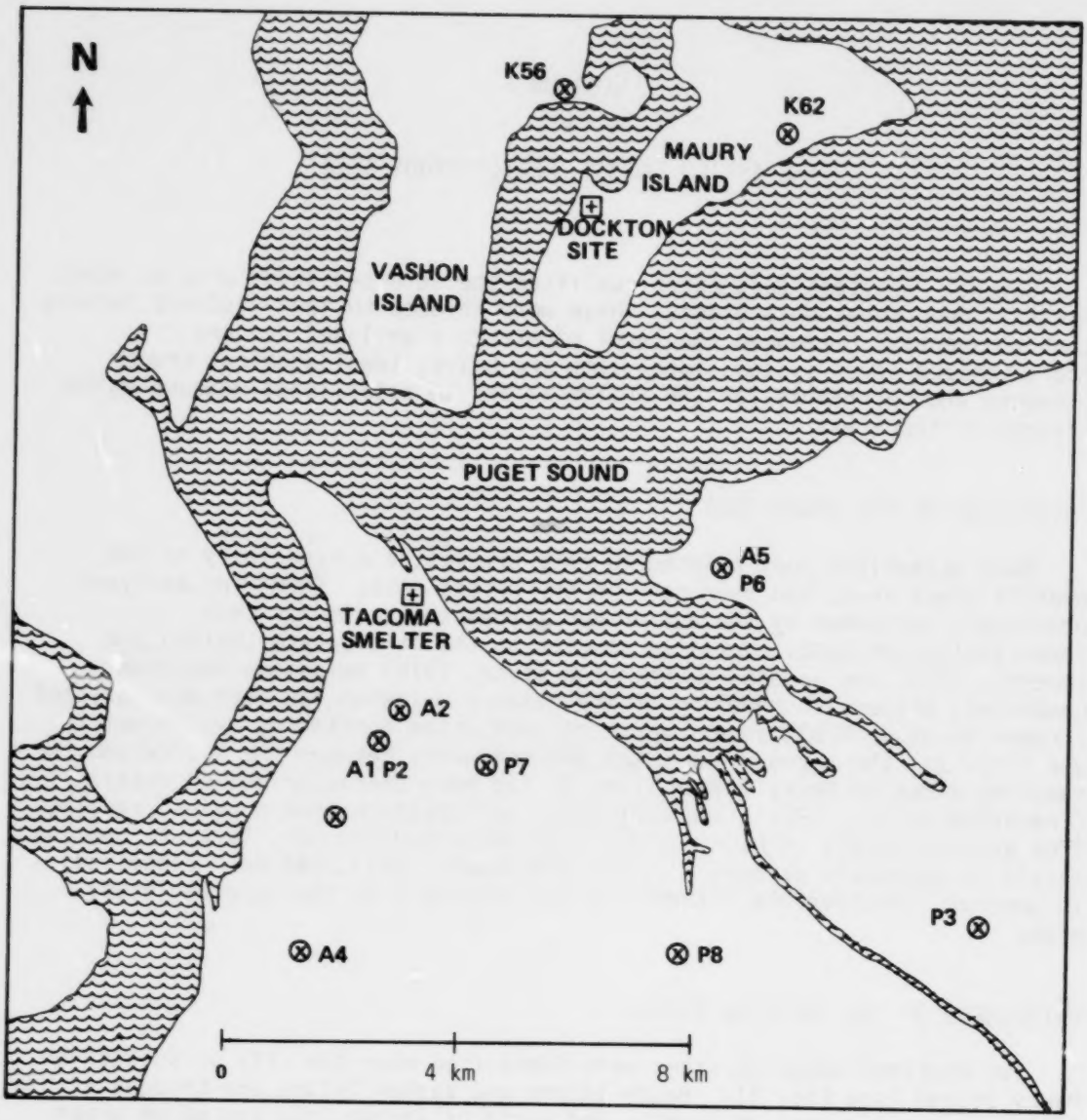

Figure 2. Air pollution monitoring network surrounding ASARCO smelter in Tacoma

for the most part have no local anthropogenic stationary pollution sources. The prevailing winds are northerly and southwesterly, depending on the season, and both sampling sites lie within the southwesterly plume envelope of the smelter. Since Tacoma is bordered on the north by Puget Sound, the only possible path from the smelter to the sampling sites is by air transport. The sites lie about 8 kilometers (km) from the smelter, within known plume touchdown areas. In Section 7, these sites are described in detail and the trees that will be studied are illustrated.

OTHER IMPORTANT CONSIDERATIONS

The experimental techniques and the meterological considerations employed in the study are described in Sections 8 and 9. They illustate the overall importance of these parameters in the demonstration project. In Section 10, the experimental results are discussed.

SECTION 6

THE HISTORY OF THE TACOMA SMELTER

PRODUCTION AND EMISSIONS

Detailed chronologies of the arsenic production levels and the corresponding stack emission levels from the American Smelting and Refining Company (ASARCO) smelter in Tacoma were either non-existent or unavailable to the public. However, certain specific facts related to the stack emissions were known and hence enabled an evaluation to be made concerning the validity of tree-ring analysis as a method for retrospective determination of pollution levels.

The Tacoma smelter began operation in 1890 as a lead smelter. In 1902 copper smelting capabilities were added (Cramer et al., 1976; ASARCO, 1976). ASARCO bought the smelter in 1905 and used it for both lead and copper smelting until 1911 when it was converted to a copper-only facility. The smelter was used to process both copper ore and copper concentrates into blister copper. In 1915, a refinery was added to treat the blister copper produced at the smelter.

Since both lead and copper ores contain arsenic in varying amounts, it follows that arsenic could have been produced at the smelter as early as 1890. Consequently, a detailed analysis of the tree rings between 1885 and 1915 for arsenic provided valuable information about the validity of tree-ring analyses, especially concerning diffusion between the rings. An evaluation of Section 10 shows this to be true for certain species of trees.

Theoretically, arsenic emissions from the stack should have been proportional to the yearly production of arsenic, as is implied above, corrected of course for the addition of pollution abatement equipment on the stack. But ASARCO considered its production information proprietary. However, certain known facts enabled an evaluation of the validity of the method. First, some production data had been released to the U.S. Environmental Protection Agency (EPA)*. This is shown in Table 1. Second,

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*Coughlin, R. L., private communication, May, 1977

although more indirect in nature, it was known that the production levels were especially low in 1967 and 1968 due to a 9-month strike from July 1967 to April 1968. Because the arsenic in question in this project was suspected of being incorporated into the tree structure during the spring growth portion of the yearly cycle, the 1968 (or 1969, depending on the lag between stack emissions and appearance in the tree) tree rings should have been low in arsenic. A similar situation should have existed in the 1959-60 period where again a strike of many months duration lowered production and emissions levels considerably. Again, the evidence presented in an evaluation of Section 10 indicates this is indeed true.

TABLE 1.

TOTAL PRODUCTION FOR THE TACOMA ASARCO SMELTER REFINERY, 1971-75 (SHORT TONS)

Year	Material processed	Smelter Cu output	Refined Cu output	As_2O_3 output
1971	380×10^3	88.2×10^3	NA	9.8×10^3
1972	406×10^3	99.8×10^3	NA	13.3×10^3
1973	384×10^3	95.5×10^3	120.1×10^3	13.1×10^3
1974	350×10^3	86.6×10^3	117.4×10^3	9.7×10^3
1975	333×10^3	72.3×10^3	119.7×10^3	NA

Finally, the United States Bureau of Mines Annual Minerals Yearbook reported information in 1961, 1962, and 1963 (USBM, 1961; 1962; 1963) that was hoped could yield a valuable fourth set of data points that could have been utilized in the evaluation. The 1961 book reported a 17% decrease in white arsenic production (As_2O_3--nearly 100% of the arsenic produced in the United States is this species) from the 1960 level; the 1962 book reported an increase of 7 percent over 1961; and the 1963 book reports a 4-percent decrease from the 1962 production level. Unfortunately, these small changes could not be accounted for because of the variability found in the data. A detailed explanation of this can be found in Section 8. A continuing effort is underway to obtain as much white arsenic production data as possible for incorporation into future phases of the project.

CONTROL EFFORTS

The control of arsenic emissions from the smelter has been both direct and indirect. An indirect control resulted from a "shutdown" policy that ASARCO followed in the past few years. When meteorological conditions forced gaseous SO_2 concentrations around the smelter to exceed certain values, the smelter was automatically shut down. A detailed search for information on the "down time" of the smelter was not fruitful, as no records were available.* As a direct control, ASARCO started a pilot baghouse in early 1974 in order to determine the best available technology for reducing stack particulate emissions. This baghouse was completed near the end of 1976, according to ASARCO, (ASARCO, 1976) and is still in operation. No effect on 1977 emissions could be determined. To date, these two control efforts represent the total control operations that affected arsenic output from the smelter.

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*This control methodology is explained in detail by Cramer et al. (1976) but no record was available concerning the frequency of these shutdowns.

SECTION 7

THE SAMPLING SITE

LOCATION

As mentioned earlier, the two sampling sites used in this project are located on Maury Island near the town of Dockton, Washington (see Fig. 2), are in a known smelter plume touchdown area, and lie about 8 km downwind from the stack. Site No. 1 (the major site) lies to the southwest of Dockton, while Site No. 2 (a backup site) lies northwest of the town in the Dockton King County Park. Both sites are shown in Figure 3. Site No. 1 was used for the initial phase of the project for several reasons: the trees were of the desired age; several species of trees were available for incremental coring; and the trees were clustered together in a small area, with each tree having a similar environmental exposure. The trees at Site No. 2 were marginal in age, of a single species, and more widely scattered--thus, less desirable for this study. Permission was granted to the author by both landowners to collect all of the samples needed.

Site No. 1 (see Fig. 3) is described legally as: King County Property, 30-22-03, tax lot 9035, that portion of the north one-half of GL 4 measured on east line ELY of Manzanita Road, less the county road. The total size of the site is 13.27 acres (53,702 square meters (m^2)), and the five subject trees are located on the site within 100 m of each other. Figure 4d shows a southerly view of the smelter as viewed from the reference point on Figure 3.

SUBJECT TREES

Previous studies by the author indicated that Pseudotsuga taxifolia (Douglas Fir) trees provided adequate yearly sample sizes and reasonable pollutant sensitivities for an arsenic analysis in individual tree rings. Unfortunatley, finding these trees of the proper age (older than 1890) and in sufficient quantity in close proximity to each other was not possible in the vicinity of the smelter. Consequently, Abies grandis (Grand Fir) and Thuja plicata (Western Red Cedar) were also sampled. Table 2 describes the trees selected from study Site No. 1. This mix was considered acceptable in that a comparison between various types of trees was desired. Since the increment borer that was used for tree ring extraction was of limited length and did

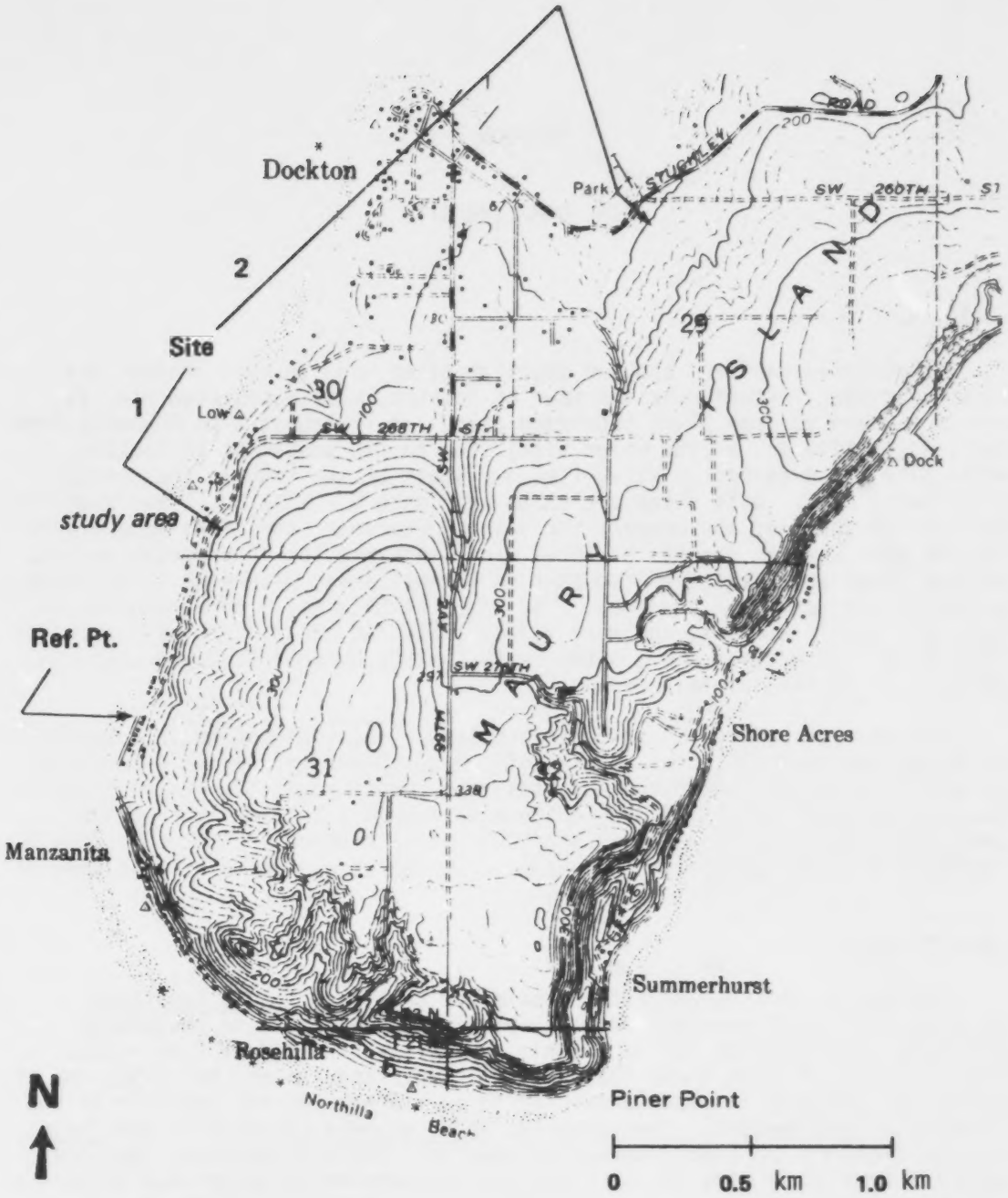

Figure 3. Topographic map of southern portion of Maury Island with site of study trees identified

(a) Trunk view of tree #1

(b) Trunk view of tree #5

(c) Trunk view of tree #3

(d) ASARCO smelter as viewed from reference point on Figure 3

Figure 4. Photographs of the study area

not penetrate to the core, the age of the larger trees was estimated. This and other sampling information will be discussed in detail in Section 8. Figures 4a, 4b and 4c show pictures of trees 1, 3 and 5.

TABLE 2. DESCRIPTION OF TREES USED IN THE ANALYSIS

Tree #	Name	Type	Age (years)	Diameter (meters)
1	Abies grandis	Grand Fir	est 130	1.3
2	Pseudotsuga taxifolia	Douglas Fir	est 100	1.0
3	Abies grandis	Grand Fir	85	0.9
4	Thuja plicata	Western Red Cedar	93	0.9
5	Abies grandis	Grand Fir	est 110	1.0

SOIL

The soil at the sampling site is called Everett-Alderwood (EwC), which is a gravelly sandy loam, usually characterized by a 6 to 15 percent slope (USDA, 1973). Both Everett and Alderwood soils are somewhat similar in that they are well-drained, dark to grey in color, and situated on a moderately strong substratum. The soil depth is typically 75 centimeters (cm) and, in the undeveloped states, covered with timber. The soil samples that were collected closely resembled this description. As will be discussed in Section 8, a 20-cm layer of litter, composed primarily of decaying leaves and needles, covered the soil.

SECTION 8

EXPERIMENTAL SYSTEMS AND TECHNIQUES

NEUTRON ACTIVATION ANALYSIS

The arsenic determinations in the tree rings were made with neutron activation analysis (NAA) at the University of Washington Nuclear Reactor Laboratory in Seattle and the Washington State University Nuclear Reactor in Pullman. The University of Washington facility has a graphite-moderated reactor with a thermal neutron flux of about 10^{12} neutrons per centimeter squared per second. Washington State University has a swimming pool reactor with a thermal neutron flux of about 10^{13} neutrons per centimeter squared per second. The U of W reactor flux proved to be marginal for the analysis of the trace amounts of arsenic found in the small tree-ring samples; however, the larger WSU re[illegible] was adequate. The WSU reactor was to be used if arsenic sensitivity pro[illegible] be a problem, but was shut down during the early stages of the project for reactor control system modifications. The use of the smaller flux reactor placed constraints on the earlier analyses and necessitated the use of two yearly rings per sample in most cases instead of one. While this limited the anticipated quantitative accuracy and affected the proposed yearly tree pollutant-smelter production correlations, good qualitative and semiquantitative conclusions could be drawn.

High resolution germanium-lithium (Ge-Li) detectors with state-of-the-art, computer-supported gamma-ray analyzer systems were used to analyze the gamma-ray spectra. All quantitative determinations for ^{76}As were performed internally by computer employing the photopeak analysis method developed by Korthoven (1970).

ELEMENTS ANALYZED

Arsenic was the only element analyzed in this study. While previous unpublished work by the author has shown that other pollutant species were also present in the tree rings taken from Pseudotsuga taxifolia (Douglas Fir) in the same general vicinity, arsenic was selected for a variety of reasons. First, it is not native to the trees in the study area. Also, it is emitted in large amounts from the ASARCO smelter (Crecelius et al., 1975), probably of the order of 2×10^5 kilograms As_2O_3 per year. Third, and

equally important, natural arsenic consists of 100 percent ^{75}As which, as the target material, has a good-sized thermal neutron capture cross section of 4.5 barns; the resultant radioactive species, ^{76}As, has an ideal half-life of 26.4 hours for the analysis (Lederer et al., 1967). Typically, arsenic can be detected in concentrations as small as 1 microgram per gram (µg/g) of material with NAA. The nuclear reactions that characterize this analytical determination are,

$$^{75}As + n \rightarrow {}^{76}As + \text{capture } \gamma\text{-ray}$$

$$^{76}As \rightarrow {}^{76}Se + \beta\text{-ray} + \gamma\text{-ray (559 keV)}$$

Other higher energy gamma rays are also emitted in the ^{76}As decays, but their intensities are less than the 559-keV photopeak.

TREE SAMPLE COLLECTION

Several tree-ring core samples were collected from each of the subject trees (Table 3). Two complete sets of cores were taken from each tree and one set was retained as a U.S. Environmental Protection Agency archive. In addition, several of the cores collected were either retained as samples or used as "practice cores" to develop ring-counting, ring-separation, drying, and weighing techniques in the laboratory.

Pruning spray was employed to keep tree infection to a minimum, and a 5-millimeter (mm) diameter by 38-centimeter (cm) long stainless steel increment corer was used to extract the cores. The instrument was kept in an organic oil when not in use to eliminate metal oxidation and subsequent sample contamination. A silicone lubricant was sprayed on the corer during operation to reduce friction. Later examination showed that neither of these materials introduced contamination in the ring samples and no evidence of any elements characteristic of stainless steel was noted in the gamma-ray spectra.

All sample cores were placed in new glass tubes in the field and sealed to reduce subsequent contamination. The tubes, designed by the author, were washed in concentrated hydrochloric acid and rinsed with distilled water prior to use in the field. The cores were typically 30 cm long, since that was the maximum obtainable with the instrument. This allowed an 85- to 125-year-old sample to be taken, a range which proved satisfactory for the study.

TABLE 3. DESCRIPTION OF TREE RING SAMPLES

Sample	Type	Height above ground (m)	Location on tree (north 0°)
1-L-A	*Abies grandis*	1.4	90°
1-L-B		1.4	85°
1-L-C		1.4	95°
1-M-A		4.8	90°
1-M-B		4.8	85°
1-U-A		5.4	90°
1-U-B		5.4	85°
2-L-A	*Pseudotsuga taxifolia*	1.4	180°
2-L-B		1.4	355°
2-U-A		3.8	180°
2-U-B		3.8	355°
3-L-A	*Abies grandis*	1.4	270°
3-L-B		1.4	275°
3-M-A		3.7	270°
3-M-B		3.7	275°
3-U-A		4.3	270°
3-U-B		4.3	265°
4-L-A	*Thuja plicata*	1.4	100°
4-L-B		1.4	90°
4-L-C		1.1	270°
4-M-A		4.3	90°
4-M-B		4.3	85°
4-U-A		5.6	85°
4-U-B		5.6	90°
5-L-A	*Abies grandis*	1.4	270°
5-L-B		1.4	275°
5-M-A		4.0	270°
5-M-B		4.0	265°
5-U-A		4.9	270°
5-U-B		4.9	265°

L, M, U = lower, middle, upper sections of tree

Since most of the trees were located on a hillside with a western exposure, the majority of samples was taken from either the east or the west side of the tree so that the ladder used could be placed on reasonably level ground. The one exception was the Douglas Fir which was located on an incline with a northern exposure.

SOIL SAMPLE COLLECTION

Soil samples were collected with a 2.5-cm diameter soil corer. The length of the corer was about 15 cm, but the instrument was designed with extension arms which allowed sample cores to be taken up to 60-cm depth. In general, about 20 cm of litter overburden was present and most soil samples were collected between 20-cm and 35 cm depth. Table 4 describes the soil samples in detail. All soil samples were placed in clean, sealable polyethylene vials in the field to keep contamination to a minimum. The typical size of each sample was 2.0-cm diameter by 2.5-cm length . A stainless steel spatula was used to cut the samples to length while in the corer and to transfer them to the vials in the field. Due to the dampness of the soil, most samples remained intact until removed for drying and weighing in the laboratory.

TABLE 4. DESCRIPTION OF THE SOIL SAMPLES

Sample	Tree	Material	Depth from surface (cm)	Location from tree (m)	(north = 0°)
1-S-1	1	Litter	10 - 12.5	1.0	60°
1-S-2	1	Soil	20 - 22.5		
1-S-3	1	Soil	22.5 - 25		
1-S-4	1	Soil	25 - 27.5		
1-S-5	1	Soil	27.5 - 30		
1-S-6	1	Soil	30 - 32.5		
5-S-1	5*	Litter	10 - 12.5	0.8	270°
5-S-2	5	Litter**	20 - 22.5		
5-S-3	5	Soil	22.5 - 25		
5-S-4	5	Soil	25 - 27.5		
5-S-5	5	Soil	27.5 - 30		
5-S-6	5	Soil	30 - 32.5		
5-S-7	5	Soil	32.5 - 35		

* This core was taken midway between trees 4 and 5
** Approximately 2.5 cm of decaying bark was encountered between the litter and soil.

Needle samples were extremely difficult to obtain in that the lowest branches on most trees were over 15 meters (m) above the ground. Tree #1 did, however, have a small branch at about 7 m and a limited number of Grand Fir needles were otained. In order to have a comparison with other needles, both live needle and cone samples were collected from a small 4-year-old Grand Fir that lies about 10 m southwest of tree #2 (Douglas Fir) and about 60 m due east of tree #1. In addition, dead needles were collected from the base of tree #1 and tree #5 while collecting the soil samples. All samples were placed in clean polyethylene vials to prevent contamination.

SECTION 9

METEOROLOGICAL INFORMATION

Crucial to accurate chronological dating of past air pollutant emissions from the ASARCO smelter was a complete record of local meteorology for the period of concern. These data were needed to accurately define dispersion from the stack to the site, and to establish a normal climatological-growth relationship for trees at the site. This relationship was needed for two reasons: to ensure that trees at the site, which is an area of wet climate and lack of temperature extremes, do reflect past climatic changes, and to ensure that the samples taken from the trees reflect normal growth patterns unaffected by local anthropogenic effects.

Since complete records of temperature, precipitation, and wind existed for Tacoma, Seattle, and Vashon Island from 1890 to the present, the author believed that qualitative relationships could be established for related tree-ring concentrations and stack emissions. However, many of the meterological parameters needed to accurately define stack plume dispersion were not available. Furthermore, the vast amount of data needed to verify the climatological-growth relationship for the Puget Sound area did not exist at the start of the project, thus creating a problem from the outset.

The analytical sensitivity for arsenic became a problem early in the analysis; therefore, full-scale dispersion modeling was not required to interpret the data and a simpler evaluation was made. The relative freedom of the study area from localized weather events made it possible to extrapolate with good reliability the available Tacoma, Seattle, and Vashon Island climatological data, thus providing the necessary weather/climate descriptors for the study area. From this, qualitative estimates of the yearly tree growth and yearly deposition of arsenic were made. A comparison of the growth estimates with the weights of the specific rings was made in order to evaluate the accuracy of and verify qualitatively the climatological-growth relationship.

CLIMATOLOGICAL DATA

Temperature and precipitation data for Tacoma for the period 1930-1960 were taken from Phillips' climatological summary (Phillips, 1960). Table

5 lists the maximum, minimum, and average temperature by months as well as the record maximum and minimum temperatures for each month of the period denoting the year in which they occurred. An evaluation of the annual results at the bottom of the table shows 1955 to be a year of extremes in temperature, an important fact that will be discussed later.

Table 6 lists the mean monthly precipitation for the 1930-1960 period along with the maximum and minimum monthly averages for the period, and the monthly 24-hour maximum. The significant anomaly is the 47.9 cm of precipitation which occurred in December 1933. This is also important and will be discussed later on. The tabulation of 24-hour maximum precipitation reinforces the previous statement that 5 cm of rain in 24 hours is a heavy rainfall for the area. Figure 5 shows the annual precipitation for the study area, along with the 10-year running mean for the years 1893-1970.

TABLE 5. TEMPERATURE STATISTICS (°C) FOR TACOMA, WASHINGTON FOR THE PERIOD 1930-1960

Month	Daily maximum	Daily minimum	Monthly average	Record high	Record low
Jan.	7.2	1.2	4.4	19.4 (1935)	-12.2 (1950)
Feb.	9.4	2.6	5.9	22.8 (1938)	-11.7 (1950)
Mar.	11.3	3.7	7.5	22.8 (1934)	-7.8 (1955)
Apr.	15.0	5.8	10.4	30.0 (1934)	-4.4 (1955)
May	18.3	8.5	13.4	32.8 (1936)	-1.1 (1955)
June	20.5	10.9	15.7	36.1 (1955)	2.8 (1955)
July	23.4	12.6	18.0	35.6 (1958)	5.6 (1957)
Aug.	23.0	12.7	17.8	35.0 (1936)	7.8 (1935)
Sept.	20.1	10.8	15.4	31.1 (1944)	2.8 (1948)
Oct.	15.5	7.8	11.7	27.8 (1931)	-1.1 (1935)
Nov.	10.6	4.3	7.5	20.6 (1949)	-13.3 (1955)
Dec.	8.6	3.1	5.8	18.3 (1934)	-10.0 (1932)
Ann.	15.2	7.1	11.2	36.1 (1955)	-13.3 (1955)

TABLE 6. PRECIPITATION STATISTICS (cm) FOR TACOMA, WASHINGTON, FOR THE PERIOD 1930-1960

Month	Mean total	Monthly maximum	Monthly minimum	24-hour maximum
Jan.	13.6	24.3 (1953)	1.7 (1949)	6.9 (1935)
Feb.	10.6	18.6 (1932)	3.9 (1934)	7.9 (1951)
Mar.	9.7	18.1 (1950)	4.6 (1944)	5.5 (1948)
Apr.	6.0	13.4 (1938)	0.6 (1955)	3.5 (1937)
May	4.1	11.2 (1948)	0.4 (1947)	2.9 (1948)
June	3.7	14.2 (1946)	0.2 (1951)	5.0 (1936)
July	1.9	7.6 (1948)	0.0 (1958)	2.7 (1948)
Aug.	2.1	5.7 (1948)	0.2 (1955)	5.0 (1936)
Sept.	4.5	10.0 (1933)	0.5 (1942)	5.4 (1945)
Oct.	9.7	22.4 (1947)	1.3 (1936)	6.1 (1934)
Nov.	12.6	24.8 (1937)	2.0 (1952)	7.0 (1937)
Dec.	15.6	47.9 (1933)	5.0 (1930)	6.3 (1933)
Annual	94.1	47.9 (1933)	0.0 (1958)	7.9 (1951)

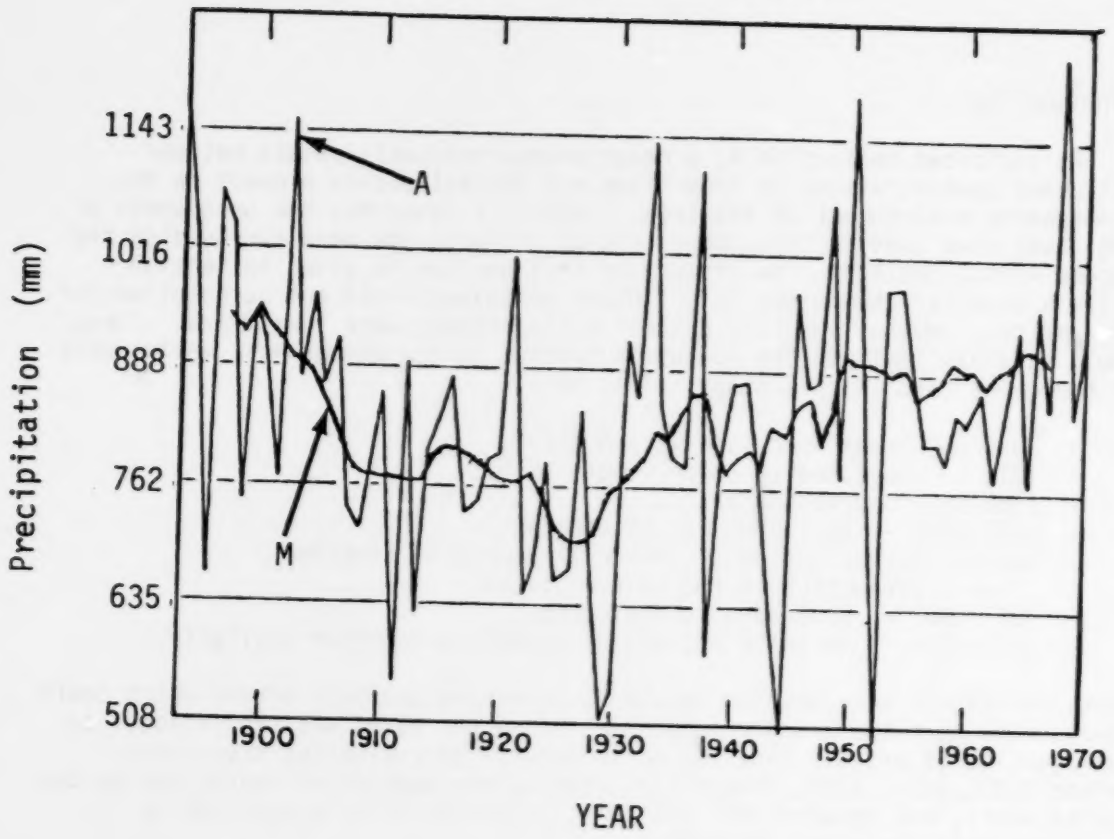

Figure 5. Annual precipitation (A) and 10-year running mean (M), 1893-1970

SECTION 10

EXPERIMENTAL RESULTS AND CONCLUSIONS

INTRODUCTION

As indicated in Section 4, a relationship evidently exists between pollutant concentrations in tree rings and the pollutants present in the atmospheric environment of the tree. Section 5 describes the uniqueness of the study area used in this demonstration project: the area surrounding the Tacoma ASARCO Smelter. The history of this smelter is given in Section 6. While a detailed chronology of pollutant emissions could not be compiled for the smelter, several specific phases in its history were identified. These could possibly indicate the pollution present in the atmospheric environment of the trees used in this study. They were:

- 1890 -- began operation as a smelter,
- 1911 -- switched to copper smelting,
- 1930's -- depression years,
- 1959-1960 -- shut down during strike,
- 1965 -- became the only commercial source of arsenic production in the United States,
- 1967-1968 -- shut down during strike,
- 1971-1974 -- definite records of arsenic production available.

These indicators were used to develop a tree-ring analysis scheme which could demonstrate that the arsenic concentration in the rings was proportional to the ejection of arsenic into the environment. By evaluating tree rings before 1890, after 1890, around 1911, during the depression years, during the strike years, and between 1971 and 1974, evidence could be gathered to correlate with the above indicators.

In addition to this, Section 4 also identified several factors that could adversely affect the interpretation of the experimental results. These were:

- diffusion between rings,
- soil leaching and uptake effects,

- direct uptake from the air by needles, and
- meteorological variation.

Other possible adverse effects could be that:

- different tree species exhibit differing effects, and
- different trees of the same species have different uptake patterns.

The tree rings contained the needed information. If diffusion between rings was taking place, arsenic should be found in rings formed before 1890. If soil leaching and uptake were problems or if direct uptake from the air was occurring, one might note differences in arsenic concentrations in the rings as a function of height in the tree. Finally, if species effects were important, or if different trees of the same species presented a problem, the chosen tree mix (three Grand Firs, one Cedar, and one Douglas Fir) should answer these questions. In order to accomplish this and check for method validity, the six specific regions of interest based on the history of the smelter were evaluated.

EXPERIMENTAL RESULTS

A detailed evaluation of the increment cores indicated that the preferred cores were from tree #2, the Douglas Fir. They were by far the largest individual rings, typically about double the weight of the Grand Fir and Western Red Cedar. Here, individual rings could be analyzed at the University of Washington, whereas in all other trees, 2 years of growth per sample were required to have sufficient arsenic activity for counting. Unfortunately, the center of the tree was decomposed and only samples dating back to 1937 could be obtained. The best tree was #5, a Grand Fir. It had the most clearly defined rings; its A and B cores and its lower, middle and upper cores matched reasonably well (see Fig. 6). Consequently, it was selected as first choice. Tree #1, a Grand Fir and the largest tree in the group, had extremely narrow rings and had little similarity in adjacent rings as a function of height in the tree. Since arsenic sensitivity was a major problem and ring counting was almost impossible in the earlier years, most of the tree #1 samples were saved as archives for future evaluation. One set of rings was analyzed at Washington State University, with the higher-neutron-flux reactor, evaluating individual rings between 1954 and 1977. This allowed a detailed evaluation of both of the strikes. Similar ring-counting problems were encountered with tree #4, the Western Red Cedar, and tree #3, a smaller Grand Fir, especially in the earlier years. Patterns of similarity could be noted in certain years however, and usually the years following 1940 could be counted with confidence.

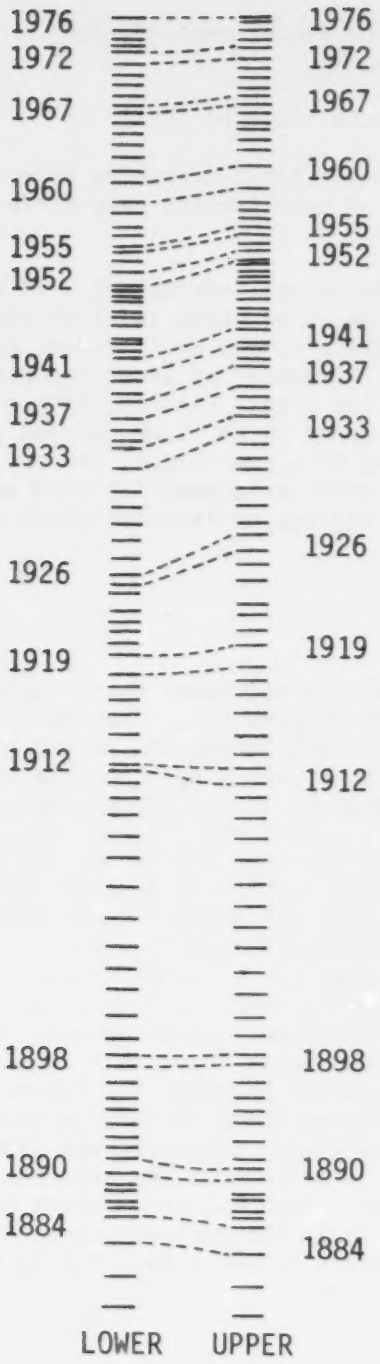

Figure 6. Comparison of upper and lower tree rings - tree #5

It is important to note here that the cores could not be mounted and polished to aid ring counting in the traditional manner because this would have introduced contamination in the rings. In the future, duplicate cores (approximately 1 cm apart) will be taken and one sample will be used for ring counting in the traditional manner and the other will be used for chemical analysis.

For this study the cores were placed on clean white paper and patterns or ring maps (Fig. 6) were constructed for each core. A sharp-pointed knife was used to roll the cores back and forth as an aid in ring identification. As was noted above, great difficulty was encountered and undoubtedly led to ring-counting errors, except for tree #5 which was far easier.

The cores were placed on clean paper and covered with Handi-Wrap[R] so that they could be cut with the sharp-pointed knife without direct handling. The Handi-Wrap[R] also kept the small individual samples from moving once they had been cut. The cuts were made along the lines separating yearly growth. The individual samples were then placed on laboratory spot-test trays that were properly labeled, transferred to the drying ovens, and weighed to constant weight. As indicated earlier, several test cores were employed in developing the technique. After weighing, the ring samples were transferred to clean polyethylene vials and irradiated in the reactor. After irradiation the samples were transferred to clean unirradiated vials and counted.

The experimental results of the study are shown in Tables 7 through 10. The concentrations were determined by comparing the sample activities to the activity of arsenic standards that were irradiated simultaneously. The standards used at the University of Washington (Table 7 data) were As_2O_3 standards prepared by the author. The standards used at Washington State University (Table 8 data) were National Bureau of Standards Orchard Leaves (SRM-1571) containing 14±2 μg/g arsenic. Special sample holders were used to ensure reproducible geometries during both irradiation and counting at both laboratories. Traditional gamma-ray standards, e.g., ^{137}Cs, ^{60}Co, ^{65}Zn, ^{57}Co, and ^{22}Na, were used to calibrate the gamma spectrometers each day. In order to ensure that each sample was exposed to a similar neutron flux, a cluster of 11 samples was the maximum possible at the University of Washington. At Washington State University, three levels were used and iron-flux monitors were employed to account for flux differences. This allowed 24 samples to be irradiated at once. Since the University of Washington reactor building was open only 8 hours per day and all 11 samples had to be counted, counting times were limited to a maximum of 40 minutes. No time restraint was necessary at Washington State University and all 24 samples were counted consecutively for 1-hour per sample. The first irradiations on tree #5 were of 1-hour duration and 1-day cooling to

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[R] Registered trade name

TABLE 7.

ARSENIC CONTENT IN STUDY TREES (MICROGRAMS As/g Wood)

	Year	Samples 5-L	5-M	5-U	4-L	4-M	Year	Sample 3-L	Year	Sample 2-L
	1886-87	---	---	---	20.9	3.30	1886-87	30.7		
	88-89	---	---	---	7.0	4.82	88-89	13.0		
Smelting	90-91	---	8.05	8.84						
begins	90-93	Trace	7.16	6.04	11.6	3.66	92-93	12.5		
	94-95	5.10	8.75	4.52	14.8	5.05	94-95	11.0		
	1910-11	24.5	1.32	6.14						
	12-13	22.2	3.04	2.87						
	14-15	8.88	6.77	0.3	5.51	3.27	1914-15	22.0		
	16-17	14.0	2.94	0.8	6.83	2.57	16-17	10.2		
	1920-21	12.6								
	22-23	12.0								
	24-25	16.2								
	26-27	8.18								
	28-29	10.2								
	30-31	10.7								
Depres-	1932	6.53								
sion	1933	4.62								
years	34-35	2.18								
	1957-58	18.0			8.12	0.59	1956-57	16.9		
Strike	59-60	28.7			3.13	5.78	58-59	10.7	1958	9.32
	61-62	20.3					60-61	10.3	1959	10.6
	63-64						62-63	12.4	1960	5.71
	1965	11.7	13.14	8.58			64-65	9.41	1961	3.43
	66-67	46.9	18.5	9.67			66-67	12.5		
Strike	68-69	194	11.9	5.74	22.3	5.13	68-69	9.83	1968	3.73
	70-71	47.2	57.1	6.07	43.8	6.44	70-71	9.01	1969	6.01
	72-73	113	14.3	6.96			72-73	5.05		
	74-75	27.7	69.3	15.1			74-75	11.9	1972	4.19
	76-77	28.4	36.7	12.5			76-77	17.6	1973	5.48

L, M, U = lower, middle, upper sections of tree.

to reduce ^{24}Na interference); 20-, 30- and sometimes 40-minute counts were made, depending on the arsenic activity. The remainder of the University of Washington irradiations were of 2-hour duration and 2-day cooling. This resulted in similar arsenic activity, but decreased the ^{24}Na from about 1-1/2 lifetime decay to 3 lifetimes and hence increased the arsenic sensitivity with respect to the sodium. In all cases, sodium was the main interference. A similar irradiation-cooling cycle was used at Washington

State for tree #1 samples. In all, 108 samples were analyzed at the University of Washington and 31 samples at Washington State. Six of the 108 samples were irradiated twice at the University of Washington to experimentally check the difference between 1-hour and 2-hour irradiations. Seven of the 108 samples were irradiated at Washington State to experimentally check the difference between the reactors. These results are shown in Table 9.

TABLE 8. ARSENIC CONTENT IN TREE #1, SAMPLE 1-L (μg As/g wood)

Year	As	Year	As
1954	0.393	1966	0.432
1955	0.402	1967	0.319
1956	0.488	1968	0.267
1957	0.541	1969	0.335
1958	0.313	1970	0.382
1959	0.344	1971	0.327
1960	0.441	1972	0.430
1961	0.277	1973	0.355
1962	0.249	1974	0.391
1963	0.499	1975	0.571
1964	0.338	1976	0.668

TABLE 9. ARSENIC CONTENT IN TREES #1 and #5 DURING STRIKE YEARS (μg As/g wood)

Year	5-L W.S.U.	1-L W.S.U.	
1965	0.33	0.39	
1966-67	0.44	0.38	
1968-69	1.39	0.30	Strike
1970-71	1.00	0.35	
1972-73	0.65	0.39	
1974-75	0.48	0.48	
1976-77	0.37	1.08	

Several additional irradiations were initially conducted on the extra increment cores to determine if acceptable arsenic sensitivity could be obtained from single rings. These studies indicated that at the University of Washington single rings could be evaluated only for Douglas Firs. Single rings could be evaluated for the other species only at Washington State.

Six different needle samples, one small Grand Fir cone, three soil samples and three standards, were also irradiated at the University of Washington reactor. These results are shown in Table 10. Two-hour irradiations and 2-day cooling periods were employed, but counting periods varied, depending on the activity. An evaluation of these data shows that arsenic concentrations are far greater in all of these than in the rings.

TABLE 10. ARSENIC CONTENT IN NEEDLES, SOILS AND CONES (μg As/g wood)

Sample	Description	Weight (mg)	Arsenic content
1-N-1	New needle	4.6	39,957
1-N-2	1-year old	5.1	7,588
1-N-3	2-year old	12.2	23,820
1-N-4	2-3 years old	15.2	27,368
Young Grand Fir	New needle	8.2	10,634
Young Grand Fir	Cone	105.9	46,260
1-N-D	Dead needle	3.5	92,857
5-S-1	Litter	19.0	27,437
5-S-2	Top 2.5 cm	18.1	21,833
5-S-4	7.5 cm deep	18.3	19,781

All samples were oven-dried to constant weight. Since meteorological conditions were important to the transport and rainout-fallout of the pollutants, a comparison between the rainfall in the study area and the growth (weight) of the rings was used as a first approximation to establish a simple growth-climatology correlation. This in turn was used to give an estimate of the expected atmospheric arsenic concentrations. The ring weights and the expected growth showed a good correlation.

DISCUSSION

An evaluation of the data in Table 7 indicates that in the case of tree #5 the method appears to be valid. For instance, no evidence of arsenic can be found prior to 1890 in either upper, middle, or lower section ring samples. Also, the arsenic concentration drops off during the depression years and there are corresponding decreases following the strike years (see Fig. 7). Of special interest is the fact that in the upper and middle samples, the arsenic concentration changes show a direct relation to stack changes in the same year (see strike year data in Table 7), while in the lower samples the tree change apparently lags behind the stack change by at least 1 year. This is seen to some extent in the Table 7 data for the other trees as well. The single-ring data from tree #1 given in Table 8 also show a drop in arsenic concentration for the 2 years following the 1959-1960 strike, but the decrease in arsenic for the 1967-1968 strike actually occurs during the same years (see Fig. 8). This will be discussed later.

On the other hand, an evaluation of the data from trees #3 and #4 shows that arsenic can be found in the rings before 1890. In both cases the center of the tree was penetrated during sample extractions. The importance of this is uncertain. In addition, the fact that the cores of these trees are so close to 1890 in age may also affect the results. The most probable answer is ring-counting errors. As stated earlier, a definite pattern correlation could be seen in the tree #5 samples and counting was easily accomplished. However, these patterns were difficult to establish and compare in the majority of the other trees; so counting back to 1890 could be in great error.

The decrease in arsenic concentration in tree #5 between 1910 and 1915 suggests the smelter change could have had an effect on the atmospheric concentration of arsenic. This can be interpreted to mean that either less arsenic was present in the atmosphere, or the arsenic was gradually eliminated from the soil, indicating the soil could have been saturated. However, the data of both tree #3 and tree #4, if they are accurate, show similar concentrations in the 1890's which leads one to believe saturation effects are small. On the other hand, the arsenic concentration in tree #5 is greater in 1910-1915 than in 1890-1895 which indicates a buildup. Since no arsenic production records are available from ASARCO and since no records are available that would indicate how the smelter output should have varied as it changed from lead to copper smelting, it is unclear what should have occurred. It is known that lead arsenate is a common ore of lead, but it is also known that many copper ores are also high in arsenic. One thing is clear: the expected growth during that time period is high for all of the years. Thus, decreasing arsenic in tree #5 between 1910-1915 is probably not a function of adverse growth, or meteorology.

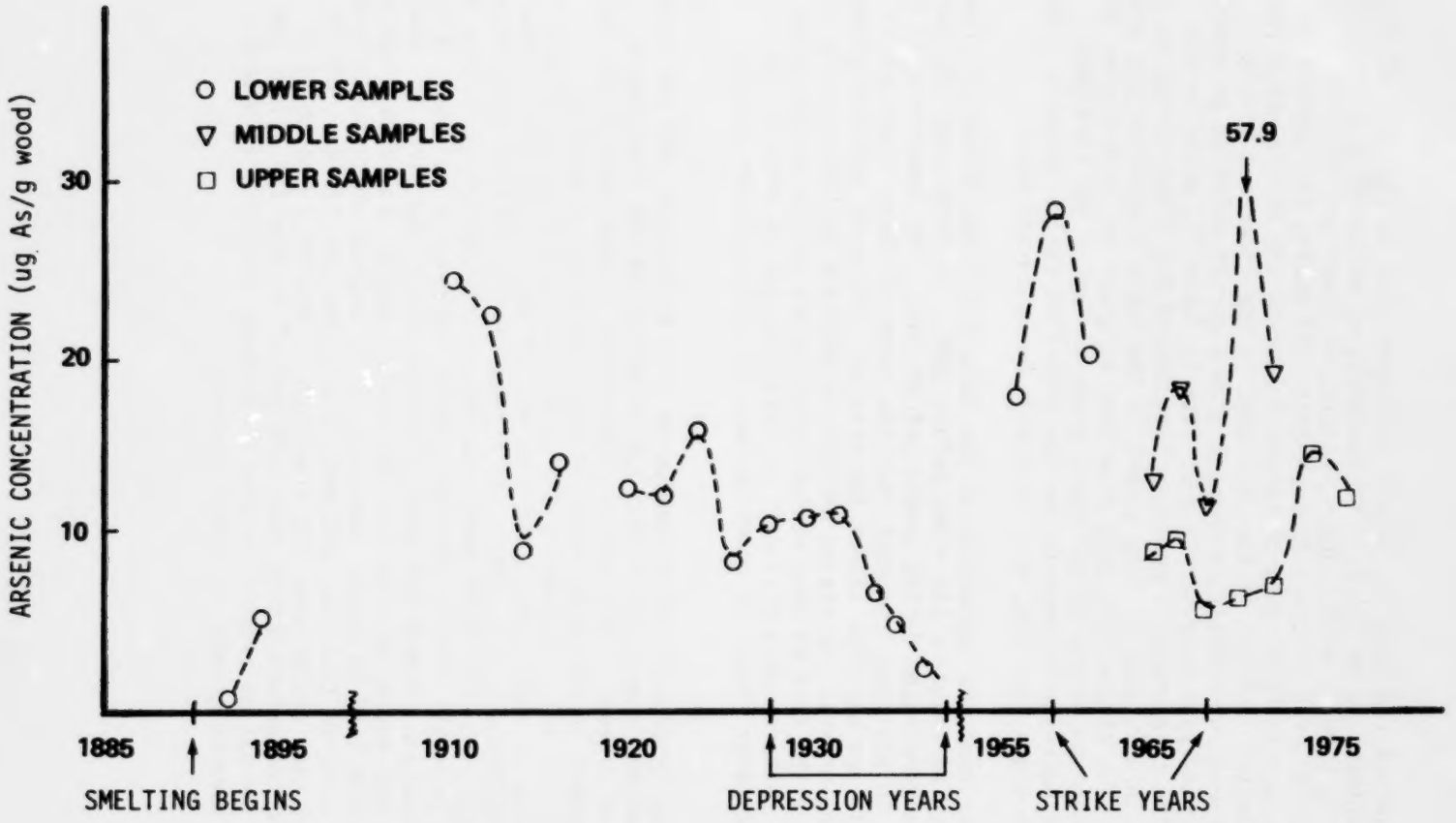

Figure 7. Yearly variation of arsenic concentration - tree #5

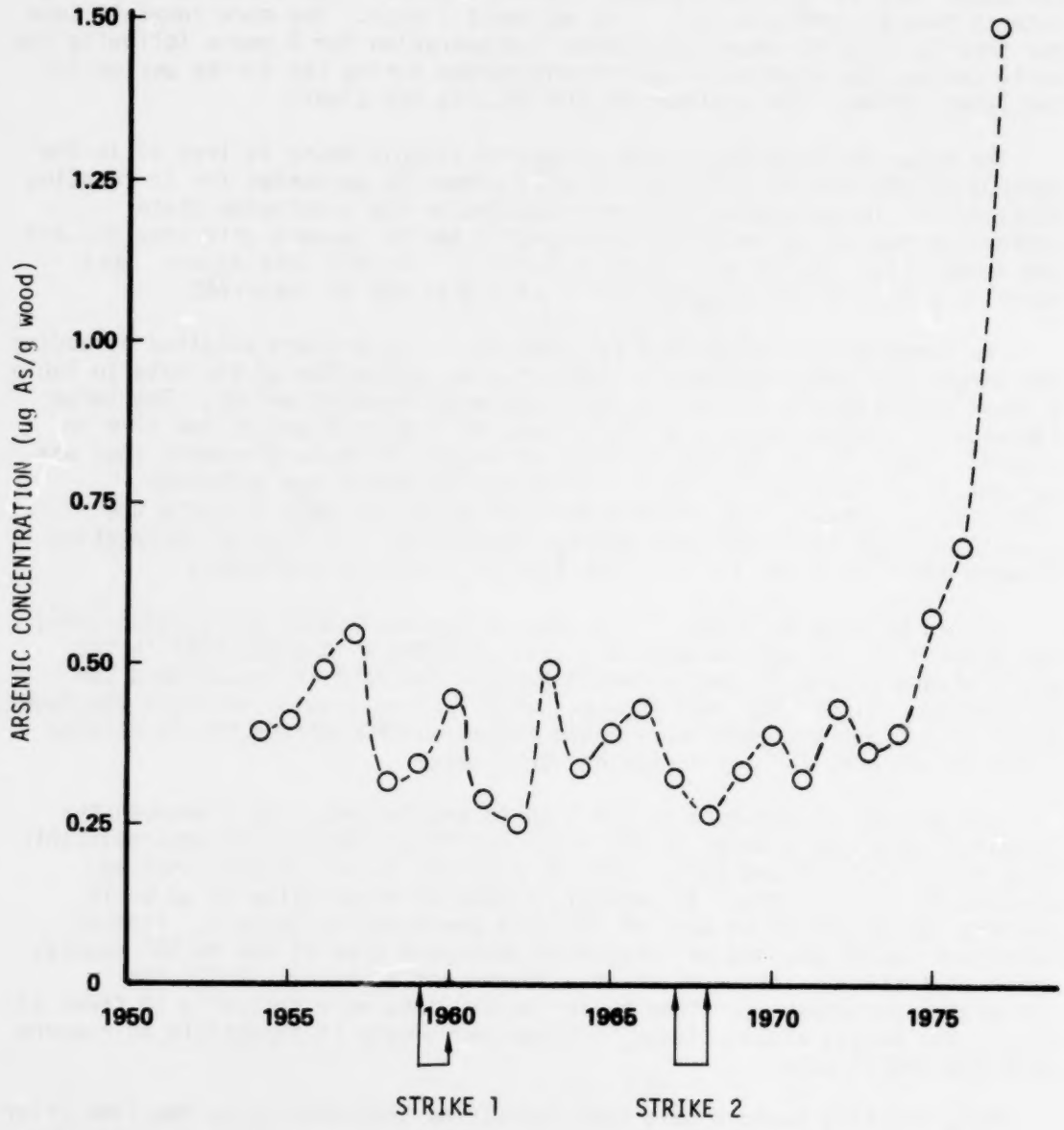

Figure 8. Yearly variation of arsenic concentration - tree #1

*U. S. GOVERNMENT PRINTING OFFICE: 1979—684-481

The strike data (1959-1960 and 1967-1968) for trees #2, #3, #4, and #5 all indicate the method is apparently valid. Consistency is noted throughout. Again the lower samples in trees #4 and #5 appear to lag behind the upper samples by 1 to 2 years. The more easily interpreted yearly ring data in tree #2 confirms that it is at least 1 year. The more complete data for tree #1 (Fig. 8) show low arsenic concentration for 2 years following the early strike, but also show low concentrations during the strike period for the later strike. The explanation for this is not clear.

The apparent exceedingly high values of arsenic found in tree #5 in the periods of 1968-69 and 1972-73 (Table 7) cannot be accounted for in counting statistics. These samples were reirradiated in the Washington State University reactor to resolve this anomally and to compare with tree #1, and the comparative results are shown in Table 9. The WSU data appear more normal for tree #5 and suggest the U of W data may be incorrect.

The comparative 2-year data for tree #1 in Table 9 were obtained by adding the single-year data reported in Table 8. An evaluation of the data in Table 9 shows that little correlation exists between trees #1 and #5. The large increase in arsenic concentration in tree #1 (Tables 8 and 9) and also in tree #3 (Table 7) can be explained as an excess of unbound arsenic that was present in the sap and may have been deposited during the extensive oven-drying process. One would expect the outer sap wood to carry the majority of the nutrients (and foreign material). The lack of correlation between the U of W and WSU data for tree #5 cannot be explained.

It can be seen in Figure 7 that during the depression years (1932-1935) the arsenic levels were exceedingly low. A cutback in production in the early stages of the depression would explain the data if one assumes the 2-year lag. Since 1930-1932 were exceedingly good growing years in the Puget Sound area (sample weights were above normal which confirms this), climate could not account for any variations this large.

The scatter in the data is too high to enable comparisons between the measured values of arsenic in the rings and direct production data available from ASARCO in 1971 and 1974. This variability is one of the limiting factors in the analysis. In general, a plus or minus value of 10 to 15 percent can be placed on most of the data presented in Table 7. Typical 40-minute counts yielded an integrated photopeak area of 100 to 500 counts, which statistially indicates about a 10-percent accuracy. While the integrated photopeaks for tree #1 in the WSU data were typically 10 times as large, the excess arsenic found in these years made it impossible to compare with the ASARCO data.

Many limiting factors have been identified that need to be resolved prior to validating this method. The limited number of trees evaluated is far from the number that should be checked. At least 10 to 20 cores should be

evaluated in order to increase accuracy, and dendrochronologists generally select no less than 20 cores in a particular area. On the other hand, other equally important, unscientific factors were identified that made the method validation equally difficult. Since sensitivity is a problem, the extraction of larger bore samples would aid in decreasing this limitation. Unfortunately, larger samples are harder if not impossible to obtain. Since most trees that could be used in analyses of this type lie on private property, permission must be obtained in order to sample them. The author found this permission hard to obtain. After considerable time, some individuals could be interested in becoming part of the study--as long as small bore samples were to be taken. No one wants 1.5 to 2-cm cores taken from his trees, especially when it is known that the larger holes need to be plugged to prevent serious infection.

CONCLUSIONS

Despite the noted problems, the available evidence favors this method. Although the results indicate that arsenic sensitivity is far less than that required to develop a quantitative theory, the experiments did show that changes in smelter production can be related to changes in tree pollutant concentrations. Further phases of the project should eliminate many problems and lead to an analytical validation.

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